特　許　庁

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特許出願公告

# 特　許　公　報　昭31-7808

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（全3頁）

## 連続的に金属チタニウムを製造する方法

### 図　面　の　略　解

図面に示すものは本発明実施の一態様を例示した縦断面図である。

### 発明の詳細なる説明

本発明はアルカリ金属或はアルカリ土金属の単味又は混合物の液体を常温又は比較的低温に於て四塩化チタニウムの液体或は蒸気と共にノヅルより同時に反応室へ噴射し、その反応熱のみにより還元剤の塩化物の融点以上のほゞ700℃～900℃の低温で還元反応を行はしめ、スライム状で生成した塩とチタニウムの混合物を鎔融塩下へ収集し、タツプ装置を加熱又は冷却することにより之を真空加熱炉へ移し真空蒸溜に附することを特徴とする連続的金属チタニウムの製法に係るものである。

即ち本発明に於ては、アルカリ金属或はアルカリ土金属の単味又は混合物を液体として四塩化チタニウムの液体或は蒸気にアルゴンを混じ或は混じないで同心二重管のノヅルを通じ同時にアルゴン等の不活性ガス気圏の反応室に霧状乃至瓦斯状として噴込み還元反応を起さしめるのであるが、之の場合金属還元剤の融点は下表の通りであるから、

融　点

| | Mg | Ca | Na | K |
|---|---|---|---|---|
| 単　味 | 650℃ | 850℃ | 97.5℃ | 63.5℃ |

合　金
- Na・K合金
  （50℃以下で液体である合金の範囲）
  Na　3～75%
- Ca・Mg合金
  （500℃以下で液体である合金の範囲）
  Ca　75～82%
  （600℃以下で液体である合金の範囲）
  Ca　8～23%　70～85%

尚食塩の直接電解で得られるNaはCa1%前後を含有するがこの融点は150℃附近である。

之等は常温乃至600℃以下の温度で反応室へ導入することが出来るし又反応開始はアルカリ金属或はアルカリ金属を多く含む合金を500℃以上に加熱して導入することにより自然着火せしめ。尓後その反応熱により反応室内の温度は還元剤の塩化物の融点以上の700℃～900℃附近に保持する。この反応によつて生成された金属チタニウムと鎔融状態の塩或は混合塩を700℃～800℃程度に保持された収集部へ落下せしめ夫々の比重差によつて金属チタニウムと塩の混合物を鎔融塩の底へ沈澱せしめる。斯くして収集部へ溜つた鎔融塩とその底に貯つたスライム状の金属チタニウムを各取出口より取出す。その際金属チタニウムはタツプ装置の加熱により真空加熱炉の中に流出させ更に之の真空加熱炉を1200℃～1300℃に加熱して塩及未反応の金属を蒸発除去し、粉末金属チタニウムのみを凝集採取するものであるが、前記真空加熱炉を他に用意されたものと交互に取替へて還元反応を中絶することなく連続的に金属チタニウムを生成し且採取するものである。

従つて本発明によれば、金属チタニウムの生成反応を行はしめるに当り反応物質である金属還元剤並に四塩化チタニムウを極めて低い温度で反応室へ供給することが出来るし、反応開始は鎔融金属の噴射による自然着火により行はれ且尓後の反応に必要とされる熱源は反応熱のみを利用すれば足り而もその温度の調節は反応物質の噴射量を調節することにより自由に調整出来、更に生成された金属チタニウムは鎔融塩中に混じスライム状で鎔融塩下に貯溜されるので之が取扱いも容易である許りでなく反応室内壁より異物の混入も防ぎ得る等連続的に純度の高い金属チタニウムを容易且経済的製造することが出来るのである。

次に本発明の方法を図面について説明する。

先づ本方法に於て使用する金属チタン還元炉の

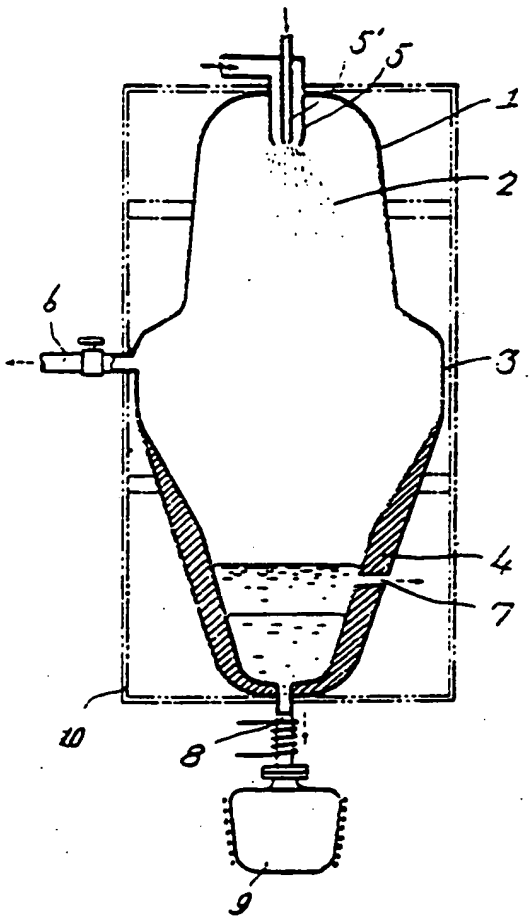
一態様に付きその概要を述べれば耐熱性を有する金属又は合金例へばステンレス、チタン或はチタン合金等にて炉壁1を作り炉の上部を反応室2とし中央部は反応生成物の落下速度を小ならしめるため炉腹3を拡げ下部は反応生成物の塩と鎔融状態に保つために保温されている炉底部4は反応生成物が収集される様に炉幅を狭くする。炉頂より四塩化チタニウムの液体（又は蒸気）を還元剤の液体と共に同時に噴射する同心円筒状のノヅル5，5を設け、炉腹部3に炉内の圧力の調節及気圏の置換のため管6を取付ける。炉下部には鎔融塩を取出すタツプホール7とスポンヂチタンの泥状沈澱を取出すタツプ装置8を取付けこのタツプ装置は導管の加熱又は冷却によつて沈澱物の真空加熱炉9への導入を始めたり止めたりする。之の炉全体を支持装置を兼ねた鋼製の殻10に入れ炉内のガス圧と該殻内のガス圧を平衡させることにより還元炉材質の耐酸化、耐圧性を保たしめるものである。

還元炉内容積50l ボンベ状の炉体頂部に四塩化チタニウムとナトリウム—カリウム合金(Na50%)とを噴出するノヅルを設け炉内の気圏を管6を以てアルゴンガスに置換した後、先づ四塩化チタニウムを霧状に噴射し次で500℃ に加熱鎔融された金属ナトリウム—カリウム合金を吹込み自然着火させ炉内温度を900℃ 附近に保持する様に噴出量を調整して還元反応を続行し炉底部に鎔融塩と粉状チタニウムとの混合物をスライム状で鎔融塩下に収集せしめ800℃ まで加熱したステンレスのタツプ導管を通じてスライム状態のまま下部の真空加熱炉に導き、次いでタツプ導管を水冷して導管中の塩を凝固せしめ反応生成物の流入を中止せしめる。次に真空加熱炉に於て1200℃～1300℃に加熱して鎔融塩として残留している塩化ナトリウム及塩化カリウムを蒸発させ之を排気管11を経て凝縮装置に導き同時に炉内のスポンヂチタンを凝集安定せしめ、次いで真空加熱炉を冷却して金属チタニウムを取出す。之の間に使用した四塩化チタニウム800g、ナトリウム—カリウム合金530gに対し得られたチタンスポンヂは172g である。尚真空加熱炉は順次交互に使用して連続的に反応は経続せしめるものである。

## 特許請求の範囲

本文に詳記し且つ図面に示すように、不活性ガス気圏の反応室内へ四塩化チタニウムと還元剤とを吹込んで反応させ、金属チタニウムと塩とを生成して金属チタニウムを製造する方法に於て液体状態のアルカリ金属或はアルカリ土金属の単味若くは混合物を常温乃至700℃ に加熱したものと四塩化チタニウムの液体或は蒸気とを同心円筒状のノヅルより同時に反応室へ噴射して自然着火せしめその反応熱のみにより反応室内の温度を還元剤の塩化物の融点以上のほゞ700℃～900℃に保持し生成したチタニウムと塩との混合物をスライム状で鎔融塩下へ集収し、タツプ装置を加熱又は冷却することによりこれを真空加熱炉へ移し真空蒸溜を施すことを特徴とする連続的に金属チタニウムを製造する方法。

特許出願公告
昭31—7808



English translation of JP-B S31-007808

# Method for continuously producing metal titanium

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a vertical sectional view illustrating one embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for continuously producing titanium metal, comprising the steps of concurrently injecting a liquid of an alkaline metal or an alkaline earth metal or a mixture thereof and a liquid or vapor of titanium tetrachloride into a reaction chamber at normal temperatures or a relatively low temperature through a nozzle; allowing them to perform reduction reactions at relatively low temperature of about 700 to 900° C, which is higher than the melting point of chloride of a reducing agent, only by their reaction heats; collecting a mixture of titanium and salts produced in the form of a slime, below a molten salt; and heating or cooling a tapping device to transfer the mixture to a vacuum furnace so that the mixture is subjected to vacuum distillation.

In the present invention, the reactions of reduction are carried out by injecting, as a nebulosus or gaseous state, a liquid of an alkaline metal or an alkaline earth metal or a mixture thereof simultaneously with a liquid or vapor of titanium tetrachloride mixed with or without argon into a vapor zone of inactive gas such as argon in the reaction chamber through a nozzle composed of coaxial double tubes. In that case, since the reducing agents for metals have melting points listed below, they can be introduced into the reaction chamber at a temperature ranging from normal temperature to 600 ℃.

Melting point

| | Mg | Ca | Na | K |
|---|---|---|---|---|
| Metal mp. | 650 | 850 | 97.5 | 63.5 |

Alloy Na·K alloy

(Range of alloys being a liquid at a temperature of 50° C and below)

Na 3～75 %

Ca·Mg alloy

(Range of alloys being a liquid at a temperature of 500° C and below)

Ca 75～82 %

(Range of alloys being a liquid at a temperature of 600° C and below)

Ca 8～23 %

Ca 70～85 %

Note: Sodium produced by direct electrolysis of sodium chloride contains approximately 1 % of Ca, and its melting point is about 150 ° C.

Further, the reduction reactions may be initiated by introducing an alloy (into the chamber) to cause them self-activation, said alloy containing a large quantity of the alkaline metal or alkaline earth metal and being heated to a temperature of 500 ℃ and above. Then, the temperature in the chamber is maintained by their reaction heats to a temperature of about 700 to 900 ℃, which is higher than the melting point of the chloride of reducing agent. Then, titanium metal and molten salt or mixed salts produced by the above reactions are allowed to fall in a collecting portion kept at about 700 to 800 ℃, and the mixtures of titanium metal and the salts are allowed to respectively precipitate to the bottom of the molten salt due to difference in specific gravity. The molten salt thus precipitated in the collecting portion and titanium metal precipitated below the molten salt in the slime form are taken out through respective outlets.

In that case, titanium metal is produced by introducing the titanium metal into a vacuum furnace by heating a tapping device, heating the vacuum furnace to 1200 to 1300 ℃ to remove the salt and nonreacted metal by vaporization, and then collecting powdered titanium metal only after its agglutination. By alternately replacing the vacuum furnace with another one, it is possible to continuously produce titanium metal without interruption of reduction reactions.

According to the present invention, therefore, it is possible to supply reactants of the metal-reducing agent and titanium tetrachloride to a reaction chamber at extremely low temperatures when carrying out reactions for production of titanium metal. The initiation of reactions is carried out by self-ignition caused by injection of molten metal. Also, it is sufficient to use the reaction heats as a heat source required for reactions. In addition, the temperature control can be done freely by controlling the injection quantity of the reaction materials. Also, since the produced titanium metal is mixed with the molten salt and stored in the form of slime below the molten salt, it is easy to handle the products as well as to prevent foreign matters of internal wall of the reaction chamber from getting into the reaction products.

Thus, the present invention makes it possible to easily and economically achieve continuous production of titanium metal with high purity.

The method of the present invention will be explained below with reference to the accompanying drawing.

Firstly, one embodiment of the titanium metal reduction furnace used in the process of the present invention will be outlined below. A furnace wall 1 is made of a heat-resisting metal or alloy such as stainless steel, titanium or titanium alloy. The furnace includes a reaction chamber 2 located at an upper portion, an enlarged furnace bosh 3 located at a middle portion, and a furnace bottom portion 4 kept its temperature constant to keep salts of reaction products in a molten state and tapered toward the bottom to collect reaction products therein. The furnace is provided at it top with a coaxial double tubular nozzle 5, 5′ for concurrently injecting a liquid (or vapor) of titanium tetrachloride and a liquid of the reducing agent into the chamber from the top of the furnace. The furnace is also provided at the furnace bosh 3 with a pipe 6 for control of the internal pressure of the furnace and for replacement of atmospheres in the vapor zone.

The furnace is provided at its lower portion with a tapping hole 7 for taking out the molten salts, and a tapping device 8 for taking out the slurry of precipitated spongy titanium. The tapping device 8 allows the precipitate to start or stop the flow entering into a vacuum heating furnace 9 by heating or cooling a conduit connected thereto.

The furnace is wholly housed in a steel shell 10 serving as a supporting device and its internal gas pressure is equilibrated with that of the shell 10 to allow the furnace material to hold oxidation resistance and pressure resistance.

The nozzle for injecting titanium tetrachloride and a sodium-potassium alloy (Na 50%) is provided on the top of the furnace body like a bomb with an internal volume of 50 liters, the atmosphere in the furnace is replaced with argon gas through the pipe 6. Then, the reduction reaction is carried out by injecting titanium tetrachloride first by spraying and then injecting the molten sodium-potassium alloy heated to 500 ° C to ignite the furnace by itself, and controlling the injection quantities so as to keep the internal temperature of the furnace to the vicinity of 900 ° C.

By continuing the reduction reaction, a mixture of molten salts and powdered titanium in the form of slime is collected below the molten salt in the bottom portion of the furnace, and introduced into the underneath vacuum heating furnace through the tapping conduit as it is. Then, the inflow of the reaction products is stopped by cooling the tapping conduit with water to solidify the salt flowing through the conduit. In the vacuum furnace, the reaction products are heated to 1200 to 1300 ° C to evaporate the sodium chloride and potassium chloride remained therein as the molten salts, which are then introduced into a condensing device through a pipe 11. Simultaneously therewith, sponge titanium is agglutinated and stabilized. Then, titanium metal is taken out by cooling the vacuum furnace. Use of 800 g of titanium chloride and 530 g of sodium-potassium alloy yielded 172 g of sponge titanium. By using plural vacuum furnaces and replacing the vacuum furnace with another one, the reaction is carried out continuously.

Cited Reference 1

(JP-B S31-007808)

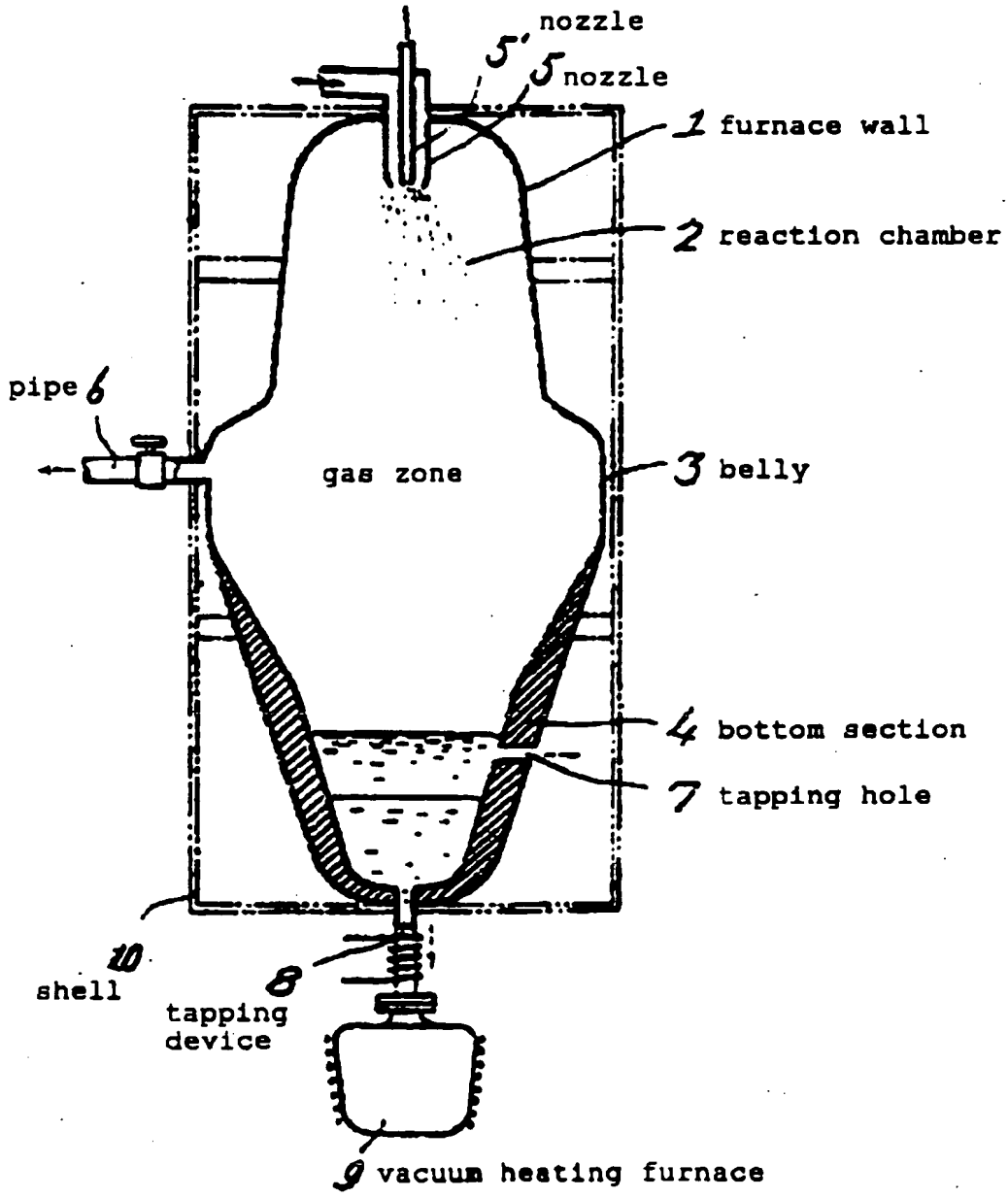
What is claimed is:

A process for continuously producing titanium by introducing titanium tetrachloride and a reducing agent into an inactive gas zone in a reaction chamber to react them with each other so as to produce titanium and a salt, said process comprising the steps of concurrently injecting an alkaline metal or an alkaline earth metal in a liquid phase or a mixture thereof, heated to a temperature of from a normal temperature to 700°C, and titanium tetrachloride in a liquid or vapor phase from coaxial tubular nozzles into the reaction chamber to cause spontaneous ignition; maintaining the temperature in the reaction chamber at a temperature of substantially 700 to 900°C not lower than the melting point of the chloride of the reacting agent by using only the reaction heat of the reduction; collecting a mixture of the titanium and the salt produced in the form of slime in a lower side under the melted salt; and heating or cooling a tapping device to thereby transfer the mixture to a vacuum heating furnace so as to be subjected to vacuum distillation.

Claim:

A process for continuously producing titanium by introducing titanium tetrachloride and a reducing agent into an inactive gas zone in a reaction chamber to react them with each other so as to produce titanium and a salt, said process comprising the steps of concurrently injecting an alkaline metal or an alkaline earth metal in a liquid phase or a mixture thereof, heated to a temperature of from a normal temperature to 700° C, and titanium tetrachloride in a liquid or vapor phase from a coaxial tubular nozzle into the reaction chamber to cause spontaneous ignition; maintaining the temperature in the reaction chamber at a temperature of substantially 700 to 900° C not lower than the melting point of the chloride of the reacting agent by using only the reaction heat of the reduction; collecting a mixture of the titanium and the salt produced in the form of slime in a lower side under the melted salt; and heating or cooling a tapping device to thereby transfer the mixture to a vacuum heating furnace so as to be subjected to vacuum distillation.

metal titanium -reducing furnace



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